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## Ion-exchange separation of metals by a single-pass method

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# Ion-exchange separation of metals by a single-pass method

## **Abstract**

A single-pass method for the ion-exchange separations of binary mixtures of metals is described, and experimental applications are presented. The method consists of complexing each of the components in the mixture with a separate complexing agent at a pH sufficient to ensure maximum coordination of the metals. The complexing agents are chosen such that the metal complexes formed are of opposite charge. The mixture is then passed through an ion-exchange resin which absorbs one species completely, allowing the other to be collected in the effluent. An anion-or cation-exchange resin is used.

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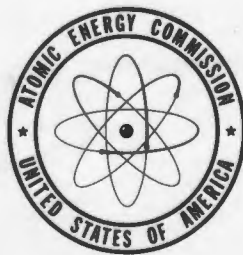
UNITED STATES ATOMIC ENERGY COMMISSION

ION-EXCHANGE SEPARATION OF METALS  
BY A SINGLE-PASS METHOD

By  
Richard T. Oliver  
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June 1958

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Ames, Iowa



Technical Information Service Extension, Oak Ridge, Tenn.

**F. H. Spedding, Director, Ames Laboratory.**

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ION-EXCHANGE SEPARATION OF METALS BY A  
SINGLE-PASS METHOD\*

Richard T. Oliver and J. S. Fritz

ABSTRACT

A single-pass method for the ion-exchange separations of binary mixtures of metals is described, and experimental applications are presented. The method consists of complexing each of the components in the mixture with a separate complexing agent at a pH sufficient to ensure maximum coordination of the metals. The complexing agents are chosen such that the metal complexes formed are of opposite charge. The mixture is then passed through an ion-exchange resin which absorbs one species completely, allowing the other to be collected in the effluent. An anion- or cation-exchange resin is used.

Sulfosalicylic acid was used to form a negative complex with iron, uranium, aluminum, thorium, zirconium, and yttrium. Ethylenediamine was used to form a positive complex with copper, zinc, nickel or cadmium. Quantitative separations of binary mixtures containing one metal from each of these groups were performed at pH values 8, 9, and 10 using Dowex-50x12,  $\text{NH}_4$  form (nuclear sulfonic cation exchange resin) and amberlite IRA-401 (quaternary amine anion-exchange resin).

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\* This report is based on an M.S. thesis by Richard T. Oliver submitted June, 1958, to Iowa State College, Ames, Iowa. This work was done under contract with the Atomic Energy Commission

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## INTRODUCTION

Analytical chemistry is the study of methods for determining elements and compounds as well as the application of these methods to practical problems. These elements and compounds can exist individually or in mixtures. In the ideal situation methods of analysis are sought that are specific for the individual component without interference from foreign ions. This situation, although occurring frequently, is still absent in a great number of analyses. For this reason the analytical chemist is continually searching for methods by which interfering constituents can be removed prior to analysis, or better yet, removed from the reacting system without being physically withdrawn, as by a masking agent. The primary purpose of this research is to use ion exchange for the separation of metal cations based upon the ability of different metals to form complexes of opposite charge with separate complexing agents. A second indirect purpose is to employ ion exchange for the separation of anions and cations in order to systematize qualitative and quantitative analysis.

Ion exchange is by no means a new process, having been used for many years for the softening of water. The literature prior to 1955 has been adequately dealt with by Kunin and Myers (58), Samuelson (74), and Osborn (70). The latter lists over 1800 references covering all phases of the

theoretical and practical applications of aqueous and non-aqueous ion exchange. A group of papers covering the theory and application of ion exchange has been published by the Society of Chemical Industry in London (33). Analytical Chemistry reviewed the subject in 1956 (56). The last two volumes of the Annual Review of Physical Chemistry (29, 101) have included review articles covering all aspects of the theory of ion exchange and ion-exchange resins as well as a large number of analytical separations. Other worthwhile reviews of the uses of ion exchangers in analytical chemistry (35-37), analytical separations (76), and general uses (54, 55, 57) have appeared during the past two years. Additional review articles are scheduled to appear shortly (4, 25).

Samuelson (74, p. vii) divides the applications of ion exchange for analytical separations into two classes:

- (1) Separations of ions from each other due to differences in exchangeability (ion-exchange chromatography).
- (2) Separations of exchangeable ions from non-exchangeable ions (single-pass method).

In the chromatographic method all ions are first absorbed at the top of the resin bed and then caused to be desorbed (eluted) differentially. This method can be subdivided into "true ion-exchange chromatography" and "the displacement of a single component." In the single-pass method the exchange-



ability of the ionic species is altered prior to loading the resin. Thus when the sample solution is being percolated through the resin bed only exchangeable ions are absorbed while the non-exchangeable ions pass into the effluent thereby effecting the desired separation.

True ion-exchange chromatography using constant elution conditions is probably best illustrated by the work of Spedding and co-workers (81-86) who completely resolved the rare earths into the pure elements. The rare earths were loaded onto a hydrogen form cation-exchange resin and eluted with a dilute solution of citric acid at a low pH. Later, the separation was improved by using a copper form resin and eluting with EDTA [ethylenedinitrilo]tetraacetic acid] (91). Macro amounts of the spectrographically pure rare earth elements were obtained. They also developed the quantitative theory involved in their work (82-85).

Holleck and Hartinger (31, 32) have investigated the dependence of the separation of the cerium earths on complex-forming elutriants and the type of exchanger employed. The use of EDTA and nitrilotriacetic acid as eluting agents were investigated by Topp (103) and Fitch and Russel (19, 20). Freiting and Bunney (21) found that lactic acid at 87°C. gave a better separation for europium and samarium than did citric acid. They also used a discontinuous gradation in eluant strength for the separation of terbium and gadolinium from europium. Vickery (107) found that the order of efficiency

of elutriants sometimes varied as a function of pH and flow rates. Choppin and Silva (14) found  $\alpha$ -hydroxy-isobutyric acid better than EDTA with respect to flow rate and better than citric and lactic acids with respect to separation factors. Mazza and Galitti (62) made a study of the influence of salt type and the speed of introduction into the column.

Ion-exchange chromatography has been used extensively for the separation of the Lanthanides from Actinides (5, 15, 95, 109). Brown and Rieman (12) separated titanium, zirconium, and thorium using citric acid. Separations of iron and gallium (38), hafnium and zirconium (8, 59), strontium, barium, and radium (60, 102), and magnesium and calcium (13) have also been reported. Anion separations of halides (6) and condensed phosphates (9) were also accomplished by ion-exchange chromatography.

The best illustration of the displacement of a single component is in the work of Kraus and his associates (39-50, 64, 67-69). In this work the absorbing characteristics of virtually all the elements in the periodic chart on ion-exchange resins were studied as a function of hydrochloric acid concentration. The usefulness of this separation is dependent upon the ability of metals to form anionic complexes whose strengths vary as a function of chloride ion concentration. The metals to be separated are absorbed onto the resin from strong hydrochloric acid solutions. The

concentration of acid is decreased slightly and the metal forming the weakest complex dissociates enough to be chromatographically eluted. The other metals either remain on the resin unaffected or are moved down the column slightly. Successive species are eluted with decreasing acid concentrations. Mixed solutions of hydrochloric and hydrofluoric acids are used for the refractory metals (39, 41-43, 46). A periodic chart showing the anion-exchange behavior of the elements in hydrochloric acid had been prepared (101). Miller and Hunter (63) have separated rhenium from aluminum and magnesium using this method. Helwig et al. (30) separated iron from cobalt, zinc and nickel. A large number of specific separations are tabulated with references in a recent review article (76).

Many interesting separations based on the displacement of a single component but employing different eluting agents have appeared in the literature. Schubert et al. (78) separated micro amounts of beryllium from calcium, uranium and copper by elution from a cation resin with sulfosalicylic acid at pH 3 to 4.5. Ryabchinkov and Bukhetarov (72) separated copper from aluminum and iron by cation exchange. Salicylate at pH 10 was used to remove copper, and hydrochloric acid was used to remove the iron and aluminum. Uranium was separated from cadmium (17) by eluting the uranium with oxalic acid followed by the removal of the cadmium with hydrochloric acid.

In order to employ the single-pass method of ion exchange the ions present in solution must have charges of opposite sign or one of the components must be neutral. Um-breit (104) was able to separate thorium from the lighter rare earths by complexing the thorium with EDTA at pH 2. The thorium formed a neutral complex with the EDTA thus allowing the thorium to pass into the effluent while the rare earths, unable to complex at this low pH, are retained by a cation exchanger. Gordon et al. (28) performed a similar separation. Using the same complexing agent, Taketatsu (97, 98) separated bismuth from zinc, cadmium, and lead at pH less than 1, and barium from lead at pH 4 to 4.5. The ion pairs cadmium-lead, iron-manganese, aluminum-beryllium, and bismuth-zinc were also separated using a suitable pH (96). Nadkarni et al. (66) removed beryllium from aluminum and iron at pH 3.5, while Bovy and Duychaerts (10) separated strontium and barium at pH 7 to 9. Alimarin and Tsintsevich (3) used tartarate at pH 9 to 10 to separate gallium from zinc. He also found that sulfosalicylic acid or EDTA could be used equally as well. Golovaty (26) was able to separate iron, aluminum, or chromium from some or all of the following metals by using a mixture of thiocyanide and EDTA: manganese, zinc, beryllium, magnesium, barium, calcium, lithium, and potassium. Thompson separated

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<sup>1</sup>Thompson, J., Ames, Iowa. Ion-exchange separation of rare earths from uranium. Private communication. 1957.

micro quantities of rare earths from a macro matrix of uranium and some iron impurities.

Many investigators employing ion exchange for separations have used the selectivity of a single complexing agent to reverse the charge on ionic species. Wheelwright and Spedding (108) separated a crude rare earth mixture into heavy and light fractions by adding a calculated amount of EDTA to complex the heavier rare earths, allowing them to pass through a cation-exchange resin. The lighter, uncomplexed rare earths were absorbed by the resin. Usatrenko and Datsenko (105) separated calcium and magnesium from iron and aluminum using tartaric acid to form anionic complexes with the latter elements. MacNevin and Crummett (61) separated the  $\text{Pd}(\text{NH}_3)_4^{+2}$  cation from  $\text{IrCl}_6^{-3}$ . Other separations using cation-exchange resins are zirconium from iron and nickel using nitric acid at pH 0.5 to 1.95 (1), molybdenum from iron in a sulfuric acid-peroxide solution (2), and rhodium from iridium using thiourea (79). Freund and Miner (22, 23) used an anion-exchange resin to separate aluminum from iron in a dilute hydrochloric, hydrofluoric acid mixture. The uncomplexed aluminum passes into the effluent while the iron-halide complex absorbs on the resin. This same separation was also accomplished with acid thiocyanate solutions (99, 100). Calcium, aluminum, and iron were resolved by a combination of a single pass of the solution through the resin in the citrate form and subsequent elution of aluminum

and iron with varying hydrochloric acid concentrations (75). The separation of iron and chromium from thiocyanate or thio-sulfate solutions has also been accomplished (106). Murthy (65) was able to remove all the vanadium from a  $\text{UO}_2^{+2}$ ,  $\text{VO}_3^{-1}$  mixture by the use of sodium carbonate and an anion-exchange resin. Small amounts of the vanadium adhered to the resin but were washed free with a carbonate solution.

The single-pass method considered in this report employs two complexing agents to form stable complexes with different cations so that the charges of the species formed are opposite in sign. A number of separations using this principle have been reported recently. Golovaty (27) performed a group separation by complexing iron, aluminum, and chromium as negatively charged phosphates and copper, zinc, cobalt, nickel and cadmium as positively charged amine complexes and passed them through a cation-exchange resin. Individual separations were also reported. Belyavskaya and Fadeeva (7) used ammonium carbonate in ammoniacal solution to separate beryllium from copper and nickel, while others used tartrate or citrate in ammoniacal solutions for a copper-lead separation (52). Ryabchinkov and Osysova (73) reported the separation of copper, aluminum, and magnesium; iron, and nickel or manganese; iron chromium, and manganese based upon the varying complexing abilities of the cations concerned with thio-sulfate, ammonia, thiocyanate, and polyphosphates.

## BASIS OF THE METHOD

The single-pass separation of a binary mixture of metals can only be accomplished when one metal exists as a cation (either complexed or free) while the other metal is an anionic or neutral complex. There are several possible ways to alter the metal cations to satisfy the above conditions:

- (1) Use a complexing agent that will react with only one of the metal cations. Examples—Polyamines react with zinc, copper, cadmium, etc., but not with iron, aluminum, calcium, thorium, etc. Cyanide reacts with zinc, but not with magnesium. This procedure generally works only in acid solutions because of precipitation of the hydrated oxides of the unreacted metal.
- (2) Use a non-selective complexing reagent that forms neutral or anionic complexes with both metals but to varying degrees depending upon pH. Examples—EDTA forms a stable, neutral complex with thorium at a pH of 2 but does not react with the rare earths. Salicylate complexes beryllium at pH 3 but not the alkali earths. Here work is generally confined to a low pH range due to formation of stable complexes with both metals in less acidic solutions.
- (3) Two complexing agents may be employed simultaneously; the first to form a positively-charged complex with one metal and the second to form a neutral or negatively-charged complex with the other. Examples—Carbonate and ethylenediamine can be used to form a uranyl carbonate anion ( $\text{UO}_2(\text{CO}_3)_3^{-4}$ ) and a

copper ethylenediamine cation ( $\text{CuEn}_2^{+2}$ ). Tartrate and 1,10-phenanthroline may be used for the separation of aluminum and iron (II). The double complexing agent procedure is useful in both alkaline and acid solutions, with the lower limit of acidity a function of the dissociation of the complexes.

Of the three ways to prepare a binary metal solution for a single-pass separation, the "double complexing agent" method is the most versatile. The first method is limited in applicability by a lack of completely selective complexing agents forming soluble complexes and the precipitation of the non-reacted metal in slightly acid or basic solutions. The second method, although very useful, is confined to mixtures in which the components form complexes with the same reagent at various pH values. Often the stabilities of the metal complexes are so close together that pH control within narrow limits is essential. The double complexing method is not hampered by precipitation of the metal hydrated oxides because these metals are also complexed. Narrow limits of pH control are avoided because most complexes are stable over a fairly wide pH range. It must be kept in mind, however, that the single-pass ion-exchange separation is a composite of all three methods, neither one functioning as a complete means of separating all metal combinations.

A basic knowledge of the complexes formed in aqueous solution for each of the components in the mixture is



necessary for the selection of reagents in the double-complexing procedure. Other than the trial and error method, a knowledge of the formation constants of the metal with each of the two reagents would be helpful. Since an excess of complexing agents is usually present to ensure complete coordination of the metals, there is the possibility that one of the metals would form a complex with each of the reagents and thus appear in both the effluent and eluant. If the absolute difference in the  $\log k$  values is less than 4, that is  $|\log k_1 - \log k_2| < 4$ , where  $k_1$  is the stability constant of the maximum coordinated complex between the metal under consideration and one complexing agent, and  $k_2$  is the stability constant for the same metal with the second complexing agent, then this is likely to happen. However, if the species being absorbed by the resin has the greater  $\log k$  then absorption by the resin would tend to give a larger apparent stability complex, resulting in the dissociation of the non-absorbed complex between the metal and the second complexing agent and the appearance of the component in the effluent being negligible. If the species not absorbed has the higher  $\log k$  value then  $\Delta \log k$  would have to be somewhat greater than 4 depending on the equilibrium absorption constants involved.

## EXPERIMENTAL NECESSITIES

## Reagents

Ion-exchange resins: Dowex-1x2, Cl form, 40-100 mesh and Amberlite IRA-401, Cl form, 20-50 mesh, both strongly basic resins of the quaternary amine type, and Dowex-50x12,  $\text{NH}_4$  form, 50-100 mesh (a nuclear sulfonic acid resin) were used throughout this work unless otherwise noted.

EDTA [disodium dihydrogen(ethylenedinitrilo)tetraacetate di-hydrate] : Sequestrene Na 2 recrystallized, as marketed by Geigy Industrial Chemicals Co.

Zinc: Primary standard zinc for melting point determination obtained from the National Bureau of Standards.

Sodium formate: Baker and Adamson reagent grade.

Sulfosalicylic acid: J. T. Baker Chemical Co. "analyzed reagent".

Hydrochloric acid: Baker and Adamson reagent grade.

Perchloric acid: Baker and Adamson reagent grade.

Nitric acid: Baker and Adamson reagent grade.

Sodium hydroxide: J. T. Baker Chemical Co. "analyzed reagent".

Pyridine: Fisher Scientific Company "certified reagent".

Ammonium acetate: J. T. Baker Chemical Co. "analyzed reagent".

Ammonium chloride: Baker and Adamson c.p. grade.

Ethylenediamine: Eastman Kodak practical grade.

Triethylenetetramine: Eastman Kodak technical grade.

Ferrous sulfate heptahydrate: Merck reagent grade.

1,10-Phenanthroline monohydrate: G. Fredrick Smith Chemical Co.

Naphthyl azoxine [7-(1-naphthylazo)-5-sulfo-8-hydroxyquinoline] : Supplied by Analytical Group II of the Ames Laboratory. The preparation and properties of this indicator are given by Fritz, Lane, and Bystroff (24).

Ceric ammonium nitrate: G. Fredrick Smith Chemical Co. reagent grade.

Lead: J. T. Baker Chemical Co. "analyzed reagent".

Water: All water used in preparing solutions and carrying out separations was distilled and deionized.

The metal ions investigated in this work were obtained from the following sources: Uranium and yttrium from the Ames Laboratory of the United States Atomic Energy Commission. All others except those specifically noted above were reagent grade laboratory chemicals.

### Solutions

EDTA (0.05 m): Dissolve 18.6 g. of reagent grade EDTA in one liter of water. Standardize against a standard zinc solution (see below) using eriochromeblack T indicator and pH 10 buffer (ammonia-ammonium chloride).

Zinc (0.05 m): Pure zinc metal is weighed out on a triple-beam balance and etched in 1:1 nitric acid-water to remove the oxide coating. The zinc is removed from the acid after 1 to 2 minutes, washed with water then acetone. It is dried, accurately weighed, and dissolved in a small amount of 1:1 nitric acid-water in a covered beaker. When all the zinc has dissolved, the solution is quantitatively transferred to a 1 liter volumetric flask and diluted to the mark with water. 3.2690 g. of zinc are required for an exactly 0.05 m solution.

Eriochromeblack T: Prepare the indicator for use by mixing the powdered dye with sodium chloride in a 1:20 w/w ratio. The indicator thus prepared is stable indefinitely. The dye-salt mixture is added to the titration vessel by means of a small spatula in an amount sufficient to give a color intensity that makes the end point easily discernible.

Ammonia-ammonium chloride buffer: 67.5 g. of ammonium chloride is mixed with 570 ml. of concentrated ammonium hydroxide and diluted to 1 liter. One ml. of this buffer solution is used for each titration on the EDTA standardization.

Naphthyl azoxine (1%): One g. of the indicator is dissolved in 99 g. of dimethylformamide.

Ammonium acetate-acetic acid buffer: 77 g. of ammonium acetate is mixed with 60 ml. of concentrated acetic acid and diluted to 1 liter. One ml. of this buffer solution is used for each titration.

Formate buffer: Approximately 0.1 g. of sodium formate is added to the titration vessel and the pH adjusted to the desired value with perchloric acid or ammonium hydroxide.

Lead reductor: The lead reductor was prepared according to the procedure of Sill and Peterson (80).

Sulfatoceric acid (0.05 m): The sulfatoceric acid was prepared and standardized according to the procedure of Diehl and Smith (16, p. 273 ).

Ferroin indicator (0.025 m): Ferroin indicator was prepared by mixing 1.4866 g. of 1,10-phenanthroline monohydrate with 0.6951 g. of ferrous sulfate heptahydrate and dissolving in 100 ml. of water.

Metal ion solutions (0.05 m): The required amount of the metal, oxide of the metal, or salt of the metal is dissolved in water or acid, as required, and diluted to 1 liter with water.

### Apparatus

Burettes: Kimble "normax" burettes were used throughout this work.

Pipettes and volumetric glassware: Kimble "exax" pipettes and volumetric glassware were used throughout this work.

Stirrer: A magnetic stirrer was used with teflon-covered stirring bars.

pH meter: All pH measurements were made on a Beckman model-G pH meter equipped with a Beckman 1190-80 glass electrode and a Beckman 1170 calomel reference electrode. Standard Beckman buffers were used to standardize the instrument.

Ion-exchange columns: The ion-exchange columns were prepared in the following way: A coarse sintered-glass disc was sealed into a 25 mm. glass tubing approximately 10 mm. from the end. The end was tapered down and sealed to a short length of 6 mm. tubing. The 25 mm. tubing was cut off 4 inches above the sintered disc and joined to a 50 mm. diameter extension tube. This larger tubing was cut two inches from the seal giving an overall height of six inches. A three inch piece of tygon tubing fitted with an eye dropper (for a tip) and a screw clamp was placed on the lower end of the column to complete the setup. A regular 60° filtering funnel with a short stem was inserted into a no. 6 l-hole rubber stopper and placed in the top of the column. This served as a reservoir for influent solutions.

Lead reductor: The lead reductor column was prepared in the same manner as the ion-exchange columns. However, a 30 inch length of 25 mm. tubing made up the stem of the column giving an overall height of 32 inches.

## EXPERIMENTAL

## Preparation of the Ion-Exchange Resins

It is essential that the ion-exchange resins for use in analytical chemistry be reagent grade materials. Rohm and Haas Co. supplies analytical grade Amberlite resins that are ready for regeneration into the desired form. The Dowex resins, on the other hand, are known to contain considerable quantities of metallic impurities (a teflon-covered stirring bar actually picked out slivers of iron from a batch of Dowex-1) and have to be cleaned prior to use. Once the Dowex resin is free from impurities it will remain reagent grade under constant use provided that the resin is properly regenerated after each use. The procedures for regeneration should be adhered to rigorously as any deviation in treatment of the resin during a series of investigations might alter the results. Samuelson (74, p. 60 ) discusses the general aspects of regeneration in his book on ion-exchange. For more specific information about regeneration for analytical purposes consult the work of Djurfeldt and Samuelson (18).

The resin is treated in two steps: First, it is freed of any contamination (the cleaning step) and second, it must be regenerated into the desired form (the regeneration step). For resins designated as analytically pure the first step can be disregarded.

### Cleaning

Approximately 250 g. of moist resin is rinsed into a large column similar to that described in the previous section. This column is 7 cm. in diameter and 30 cm. high with a coarse glass frit sealed into its base and the glass tapered to 15 mm. below the frit. A 10 cm. length of 13 mm. rubber tubing is fitted to the glass taper and a screw clamp placed on the rubber tubing. The purpose of the clamp is to control the flow of liquid from the column. The resin is backwashed to remove the fines and any other loose non-resinous material. A backwash flow rate sufficient to cause a 50% resin bed expansion was used. When the water above the resin is free from fines and all air bubbles are excluded from the column the back flow is discontinued and the water allowed to drain to within 2 cm. from the top of the resin bed. From this point on until after the regeneration step the liquid level is not allowed to fall below the level of the resin bed. A 500 ml. separatory funnel fitted with a no. 13 1-hole rubber stopper is then placed into the top of the column and filled with 1 m hydrochloric acid. The funnel stopcock and screw clamp are opened and 250 ml. of the acid is allowed to percolate through the resin at maximum flow rate. This operation rapidly replaces the water with acid. The remaining acid is passed through the resin at a flow rate of 5 to 8 ml. per min.; the rate is controlled by means of the screw clamp while the stopcock is held open. When the acid



reaches the stem of the funnel the screw clamp is closed and the process repeated with 1 m sodium hydroxide. The percolation of acid then base is continued until one liter of base is used. A final 250 ml. of acid is used to neutralize the base in the resin and one liter of water percolated through to remove any excess acid.

Passage of blank samples through fractions of the cleaned resin showed negligible titers when analyzed with cerium (IV) or EDTA according to previously described procedures. Alternative procedures are also available. Umbreit (104, p. 21) used a 10% w/w ammonium citrate solution to remove tri- and tetravalent ion contaminants. Iron was removed from anion resins by Thompson<sup>1</sup> who added 1,10-phenanthroline and hydroxylammonium chloride to a slurry of resin, which was then filtered and washed to remove excess reagents and the ferrous 1,10-phenanthroline complex.

### Regeneration

Used resin that is to be regenerated should be placed in the column and backwashed, as described above, to effect a loosely packed resin bed free of channels.

500 ml. of 3 m ammonium chloride is placed in the separatory funnel following the final water wash of the cleaning step and allowed to percolate through the resin

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<sup>1</sup>Thompson, J., Ames, Iowa. Ion-exchange separation of rare earths from uranium. Private communication. 1957.

bed at maximum flow rate. After half of the salt solution has been used the flow rate is reduced to 5 to 8 ml. per min. When the last of the ammonium chloride solution reaches the stem of the separatory funnel, the funnel is refilled with more of the same without interrupting the flow rate. This is repeated once more so that 1250 ml. of 3 m ammonium chloride has passed through the resin at the 5 to 8 ml. per min. flow rate. The flow rate may be increased if desired but at least one hour of contact time between resin and fresh ammonium chloride solution should be maintained. Finally, the resin is backwashed to remove the excess salt solution. A drop of silver nitrate added to a fraction of the backwash effluent acidified with nitric acid serves as a test for the complete removal of chloride ion. The wet resin is transferred to a wide mouth jar and the excess water decanted off. The resin is used directly from the jar with no further treatment.

#### Preparation of Ion-Exchange Columns for Separations

Dowex-lx2 and Amberlite IRA-401, both strongly basic quaternary ammonium type anion-exchange resins, and Dowex-50xl2, a nuclear sulfonic acid cation-exchange resin, all prepared as directed, were used throughout this work except where otherwise noted. For column separations, eight grams of air dried resin is weighed into a 150 ml. beaker and water is added to form a slurry. This is poured into the top of one of the

columns to which 10 ml. of water has been added. After the resin has settled the column is tapped lightly to level the resin. The height of the resin bed is measured and all columns marked with a red band at that height. The markings serve as a guide for taking approximately the same amount of resin for each separation without having to dry the moist resin and weigh it out each time. An exact measurement of the amount of resin used is not necessary in these single-pass separations. It is only necessary that the resin be in excess of the ionic equivalent in the sample solution. Next, the water level is adjusted to within one cm. above the resin bed and the filter funnel attachment inserted so that the tip of the funnel just touches the surface of liquid in the column. The pH of a wash solution  $10^{-3}$  M in both complexing agents is adjusted to the desired value and 50 ml. poured into the funnel and allowed to percolate through the resin at a rate of 5 to 10 ml. per min., the flow rate being adjusted by the screw clamp at the base of the column. When the solution level drops to the stem of the funnel an additional 50 ml. of the wash solution is added. This is repeated until the effluent pH is within 0.3 pH units of that of the influent solution. This usually requires less than 100 ml. When the proper pH conditions have been satisfied the liquid is allowed to drain to the funnel stem and the screw clamp closed. The column is now ready for use.

The preparation of resin for batch operation is somewhat simpler. The required amount of wet resin is transferred to a 150 ml. beaker and 100 ml. of wash solution added.

The pH is then adjusted to the desired value while the resin is being stirred vigorously with a magnetic stirrer. After the desired pH has been obtained the resin is allowed to settle out and the excess solution decanted off. The resin is used in this condition.

#### Preparation and Treatment of Samples

The composition of the samples is dependent upon the information sought. For example, if the exchange behavior of a single metal ion in the presence of one or both complexing agents is being studied, the other metal of the binary sample may be left out along with the second complexing agent. The preparation and treatment of binary metallic solutions will be described here; however, the treatment of all samples will be the same.

Five ml. aliquots of the 0.05 m stock solutions of each metal to be separated are pipetted into a 150 ml. beaker containing a teflon covered stirring bar. Twenty ml. of distilled water are added and the pH checked with hydrion paper. The solution should be strongly acid as a result of the manner in which the stock solutions were prepared. Thirty ml. of 0.1 m sulfosalicylic acid are then added followed by ten

ml. of 0.5 m ethylenediamine. For the cation-exchange separations two ml. of ethylenediamine are added. The mixture is placed on a magnetic stirrer, stirred, and the pH adjusted to the desired value using ammonium hydroxide or perchloric acid. Part of the solution is quantitatively transferred to the funnel on top of the ion-exchange column and allowed to pass through the resin at maximum flow rate into a 250 ml. beaker. Without interrupting the flow rate or allowing the liquid level to fall below the stem of the funnel, transfer the remainder of the sample is transferred into the funnel. The beaker is rinsed three times with the wash solution; the washings are poured into the funnel each time. Fifty ml. of water are added after the washing and the screw clamp closed when the water level reaches the funnel stem. The effluent is saved for analysis.

When the species absorbed by the resin is of no interest the resin is placed in a collection jar for regeneration at a later time. In the cation-exchange separations where the absorbed species are to be analyzed the resin is eluted as follows: fifty ml. of 3 m hydrochloric acid are poured into the funnel above the resin and percolated through the resin at a flow rate of 1 to 2 ml. per min. followed by 50 ml. of water. The eluate is collected in a 250 ml. beaker and saved for analysis.

For the batchwise separations the solution is prepared in the same manner as described above. A stirring bar and the resin prepared for batch operation are added to the

sample beaker and the contents stirred magnetically. The pH is checked while stirring, and adjusted to the desired value if any deviation occurs. The solution and resin are mixed vigorously for five minutes. The sample is removed from the stirrer and its contents quantitatively filtered using normal filtering techniques. The resin is washed several times with wash solution and all filtrates collected in a 250 ml. beaker for analysis.

### Analysis of Samples

#### Uranium

Uranium is analyzed by a method of Sill and Peterson (80) which was modified slightly. The uranium (IV) resulting from the reduction of uranium (VI) in a lead reductor is collected in an excess of ferric chloride and the resulting ferrous iron determined as described below.

#### Iron

Iron is analyzed by titration with sulfatoceric acid as described in Diehl and Smith (16, p. 276). The reduction of ferric iron is carried out in a lead reductor as described above for uranium.

#### Copper, zinc, nickel, and cadmium

These metals were analyzed by the method of Fritz, Lane and Bystroff (24).

## Data

A summary of the ion-exchange separations performed is tabulated in Tables 1 and 2. Uranium, iron, thorium, aluminum, yttrium, zirconium, and bismuth were complexed with sulfosalicylic acid while copper, zinc, nickel, and cadmium were complexed with ethylenediamine. Dowex-1x2, Cl and Amberlite IRA-401, Cl, both strongly basic quaternary amine resins and Dowex-50x12,  $\text{NH}_4$ , a nuclear sulfonic acid resin were used throughout. The anion-exchange separations were performed in batch and column operations with equal ease and flexibility. The batch technique is especially convenient since it requires no special equipment for its use. The column method was used exclusively throughout the cation-exchange separations because the absorbed copper had to be eluted prior to analysis.

The success of each separation was determined by the recovery of the metal forming a complex with ethylenediamine. For the anion-exchange separations the effluents were analyzed for zinc, copper, nickel, or cadmium (Column six, Table 1) to determine the efficiency of the separation. For the cation-exchange separations the copper was eluted from the resin and analyzed to determine the extent of separation. That a single analysis is truly a measure of the completeness of the anion-exchange separations was shown by absorption studies of uranium and iron. Sulfosalicylate complexes of these two

Table 1. Anion-exchange separations (Sulfosalicylic acid used to complex  $M_1$  and ethylenediamine used to complex  $M_2$ .)

Separation of $M_1$ from $M_2$	Resin	pH	Meq. $M_2$ taken	Meq. $M_2$ found	%Recovery of $M_2$	No. of samples
U -Zn	IRA-401 <sup>a</sup>	9	0.8850	0.8712	98.44	3 <sup>b</sup>
	Dowex-1x8 <sup>c</sup>	9	0.8850	0.8736	98.71	1
	Dowex-1x2 <sup>c</sup>	9	0.6019	0.5983	99.40	2
	Dowex-1x2 <sup>c</sup>	10	0.8850	0.8841	99.90	1
		10	2.213	2.200	99.41	1
Fe-Zn	Dowex-1x2 <sup>a</sup>	10	0.6019	0.6014	99.92	2
U -Cu	IRA-401 <sup>a</sup>	8	0.5044	0.5037	99.87	3
	IRA-401 <sup>a</sup>	10	0.5044	0.5008	99.28	3
U -Ni	IRA-401 <sup>a</sup>	8	0.4535	0.4489	98.99	4
	Dowex-1x2 <sup>c</sup>	10	0.4917	0.4892	99.49	1
U -Cd	Dowex-1x2 <sup>c</sup>	8	0.5344	0.5283	98.86	2
	Dowex-1x2 <sup>c</sup>	10	0.5344	0.5228	97.82	2

<sup>a</sup>Batchwise operation.

<sup>b</sup>A turbidity resulted when resin and solution were mixed.

<sup>c</sup>Column operation.



Table 2. Cation-exchange separations (Sulfosalicylic acid was used to complex  $M_1$  and ethylenediamine used to complex  $M_2$ .)

Dowex-50x12,  $NH_4$  in column operation was used throughout.)

Separation of $M_1$ from $M_2$	pH	Meq. $M_2$ taken	Meq. $M_2$ found	% Recovery of $M_2$	No. of samples
Fe-Cu	8	0.5044	0.5041	99.94	5
	10	0.5044	0.5085	100.81	3
	10	0.5044	0.5092	101.95	2 <sup>a</sup>
Th-Cu	8	0.5044	0.5043	99.98	4
	9	0.5044	0.5038	99.88	4
	10	0.5044	0.5111	101.33	2 <sup>a</sup>
Al-Cu	9	0.5044	0.5044	100.00	2
	10	0.5044	0.5142	101.95	2 <sup>a</sup>
Y -Cu	9	0.5044	0.5146	102.02	4
Zr-Cu	8	0.5044	0.5071	100.53	2 <sup>b</sup>
	8	0.5044	0.5308	105.24	2 <sup>b</sup>
	9	0.5044	0.4855	96.26	2 <sup>c</sup>
	9	0.5044	0.5008	99.29	5 <sup>c,d</sup>
	10	0.5044	0.5090	100.92	2 <sup>a,c</sup>
Bi-Cu	10	0.5044	0.5176	102.62	2 <sup>a</sup>

<sup>a</sup>Triethylenetetraamine used to complex Cu.

<sup>b</sup>The Zr solution used contained a minimum amount of HCl. The second pair of samples were heated prior to passing through the resin.

<sup>c</sup>The Zr solution used contained a considerable excess of chloride ion introduced as HCl to cause dissolution of the Zr metal.

<sup>d</sup>A series of 5 samples were fumed to near dryness with  $HClO_4$  prior to preparing the binary mixture for separation.

Table 3. Cation-exchange behavior of Cu and Fe on Dowex-50x12,  $\text{NH}_4$  as a function of sulfosalicylic acid (SSA) and ethylenediamine (en) concentrations

Ml. 0.05 $\underline{\text{m}}$ Cu	Ml. 0.05 $\underline{\text{m}}$ Fe	Ml. 0.1 $\underline{\text{m}}$ SSA	Ml. 0.5 $\underline{\text{m}}$ En	pH	% Recovery of Cu
0	10	20	10	10	1.84
5	10	20	10	10	101.84
5	0	10	10	10	100.00
5	0	20	10	10	100.19
5	0	0	10	10	100.00
5	0	0	10	10	100.00
5	0	10	0	10	98.85
5	0	2	0	10	99.24
5	10	30	2	10	100.78
5	10	30	2	8	100.28
5	10	30	1	8	99.88

metals are intensely colored and form sharp bands at the top of the light yellow resin bed. Effluents from these columns contained no trace of uranium or iron when the solutions were reduced in a lead reductor and titrated with cerium (IV).

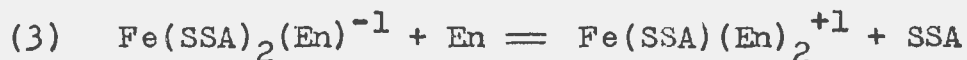
During the early stages of the cation-exchange separations high results were obtained after eluting the resin and analyzing for copper. A study was undertaken to determine

the effect of the complexing agent concentration on the absorption of iron and copper. The results are listed in Table 3. After an increase in the sulfosalicylate concentration the copper recoveries were quantitative both from binary mixtures and when copper was used alone. This indicated that a single copper analysis would be sufficient to determine the efficiency of any particular separation.

## DISCUSSION

The anion-exchange separations reported in Table 1 are best performed using Dowex-lx2 in column operation. Amberlite IRA-401 when used batchwise gave a quantitative separation of uranium from copper but only a fair separation of uranium from nickel. Cadmium was not quantitatively recovered from the effluent of a Dowex-lx2 column. Evidence is not complete enough to be able to compare the anion-exchange behavior of Dowex-1 and Amberlite IRA-401. The failure of Dowex-lx2 to effect a separation of uranium and cadmium while doing so for zinc appears anomalous since zinc and cadmium form complexes of very similar stability.

In the cation-exchange separations (Table 2) some difficulty was encountered with the first system investigated. Preliminary exchange behavior experiments were carried out on both copper and iron in the presence of their respective complexing agents. The results indicated that all the copper was absorbed by the resin and all the iron was collected in the effluent. However, when both metals and both complexing agents were mixed a high copper recovery was obtained after each separation. The formation of a mixed iron-ethylenediamine-sulfosalicylate complex is proposed as a possible explanation for the high recovery of copper. Equilibria involving iron, ethylenediamine, and sulfosalicylate are as follows:



The existence of a cationic species represented by reaction (4) is highly unlikely since iron precipitates in the presence of ethylenediamine and no trace of precipitation was observed during the experiments when sulfosalicylate was present. The singly charged cation of reaction (3) might exist and would be absorbed along with the copper-ethylenediamine complex. An increase in sulfosalicylate concentration and a decrease in ethylenediamine concentration would tend to suppress the formation of the mixed iron complexes leading to a more efficient separation. The absorption behavior of copper and iron on Dowex-50x12 as a function of the concentrations of complexing agents shows this postulate to be valid. The results for the copper-iron separation in Table 2 were obtained using a minimum ethylenediamine concentration.

Several other points concerning the cation-exchange separations are to be noted. Triethylenetetramine was used as a complexing agent for copper in a number of separations. In these separations the copper recovery was high.

Triethylenetetraamine is a slightly stronger complexing agent than ethylenediamine and would be expected to form more stable mixed complexes than ethylenediamine. This results in a situation not unlike the copper-iron system mentioned above.

The high results of the copper-yttrium separation probably indicate a weak yttrium sulfosalicylate complex. A 1:1 complex between yttrium and sulfosalicylate would be absorbed by the resin, resulting in high copper recoveries.

Zirconium-copper mixtures that were heated prior to separation showed a considerable increase in the apparent copper recovery. This may possibly have been a result of a polymerization of zirconium. Raby (71) showed that polymerization of zirconium is a possibility by preparing a fresh solution of zirconium and standardizing it immediately by (1) precipitating the oxide and (2) an EDTA titration. The results were identical. As the solution aged, however, the EDTA titer decreased while the precipitation method showed no loss of zirconium. The polymer was not reacting with the complexing agent (EDTA). Heating of solutions prior to the separation could well initiate polymerization of the zirconium. The polymerized zirconium then would not react with the sulfosalicylate and be absorbed by the resin. The 3 m hydrochloric acid used in eluting the resin is sufficient to destroy the polymer, thus allowing the zirconium to be titrated along with the copper.

An attempt to separate iron and zinc from a citrate ethylenediamine solution using a cation resin was unsuccessful while the separation using sulfosalicylate-ethylenediamine and an anion resin was successful (Table 1). Zinc was not quantitatively absorbed on a cation resin in the presence of citrate even when ethylenediamine was added. The complex stability constants for zinc and citrate are not known but are probably sufficiently strong to cause some loss of zinc through non-absorption by the resin. The formation of a zinc sulfosalicylate complex does not play an important role in the anion-exchange separations for two reasons. The first is that a large excess of ethylenediamine is present during the anion-exchange separations; this would favor the formation of the positively charged amine complex. Secondly, as the solution passes through the anion resins the sulfosalicylate concentration is reduced due to absorption by the resin. This would tend to dissociate any zinc sulfosalicylate that had formed.

The weakly basic Dowex-3 and the weakly acid Amberlite IRC-50 were investigated for possible value in separations. Dowex-3 being a weak base exchanger was of no use in a basic media. Amberlite IRC-50, on the other hand, retained copper ethylenediamine quantitatively under similar conditions. Difficulty was encountered, however, when the resin was used in batch or column operation, because the resin is not at all robust and breaks into fines under stirring. The fines

either clogged the pores of the filter or passed into the filtrate carrying some absorbed copper with them. In column operation channelling occurred during the elution step and pockets of copper were retained in the resin bed. Considerable time and eluting agent were needed to ensure complete removal of the copper.



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